



## Radiation-induced grafting of perfluorinated vinyl ether into fluorinated polymer films

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### ABSTRACT

We report herein the first successful grafting of perfluorinated vinyl ether monomer into base polymer films by simultaneous radiation method. 2-Bromotetrafluoroethyl trifluorovinyl ether (BrTFF) could be grafted into poly(ethylene-co-tetrafluoroethylene) (ETFE) films by  $\gamma$ -rays irradiation at room temperature. The grafting yield increased linearly with an increase in the dose up to 1400 kGy. The required dose for a satisfactory grafting yield, such as 20%, was as high as ca. 400 kGy probably due to low polymerization reactivity of fluorinated monomers. However, the solvent and catalyst had no positive influence for improving the grafting yield. FTIR spectra and SEM-EDS testified that BrTFF was successfully grafted into ETFE films homogeneously in the perpendicular direction. The thermal analysis of the grafted films further indicated no phase separation between poly(BrTFF) grafts and ETFE films, probably owing to high compatibility of the fluorinated grafts and base polymers.

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### 1. Introduction

It is well known that the radical polymerization of perfluorinated vinyl monomers is extremely low except a few compounds such as tetrafluoroethylene, chlorotrifluoroethylene, and hexafluoro-1,3-butadiene [1–3]. Perfluorinated vinyl ethers, such as trifluorovinyl heptafluoropropyl ether ( $\text{CF}_2=\text{CF}-\text{O}-\text{C}_3\text{F}_7$ ) (FVPE) shows similar reactivity; however, we reported recently that radical polymerization of FVPE proceeded with radical sources from  $\gamma$ -rays irradiation but not with thermal radical initiators such as AIBN and BPO. Namely, by the irradiation of bulk FVPE with 1000 kGy at room temperature under reduced pressure, the vinyl polymerization of FVPE proceeded with 97% monomer conversion to give polymeric products in a 49% yield [4].

The radiation-induced grafting is one of the most effective methods for the introduction of active functional groups into the graft polymer chains in membranes. In our past work, some polymer electrolyte membranes have been developed by the radiation grafting of styrene derivatives such as styrene, vinyltoluene and divinylbenzene into fluorinated polymer membranes, followed by sulfonation with chlorosulfonic acid. Some properties

have been improved obviously compared to Nafion<sup>®</sup> membranes [5–7]. Although fluorinated polymers have excellent chemical and physical properties for industrial applications such as brine electrolysis membranes and polymer electrolyte membranes for a fuel cell, radiation-induced grafting of perfluorovinyl monomers including perfluorovinyl ethers has not been reported [8,9].

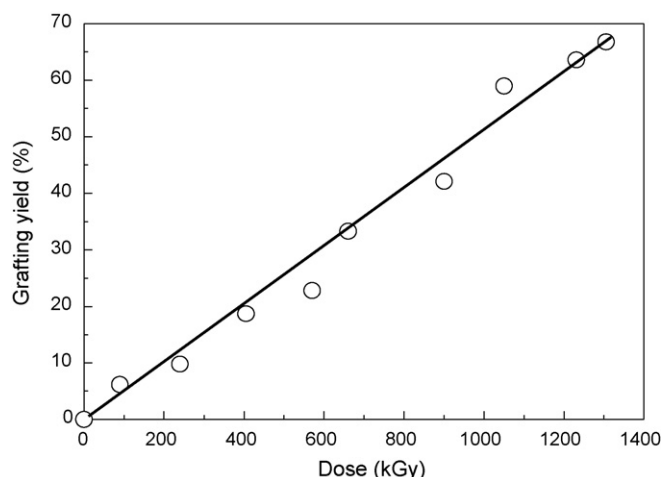
From the above situation, we have attempted the radiation-induced grafting of perfluorinated vinyl ether into poly(ethylene-co-tetrafluoroethylene) (ETFE). In this study, we selected 2-bromotetrafluoroethyl trifluorovinyl ether (BrTFF) as a monomer because bromine of BrTFF acts as a functional group, being utilized for further sulfonation or atom transfer radical polymerization.

### 2. Results and discussion

#### 2.1. Simultaneous radiation-induced grafting of BrTFF into ETFE films

A simultaneous radiation-induced grafting was investigated for the grafting of BrTFF into ETFE films. Fig. 1 shows the results of the grafting of BrTFF into ETFE films as a function of the dose at room temperature. The grafting yield (GY) increased linearly with an increase in the dose up to 1400 kGy. The area of the resulting film increased with proceeding of grafting; this increase suggested that the graft polymerization began on the surface of the film and proceeded internally with a progressive diffusion of the monomer

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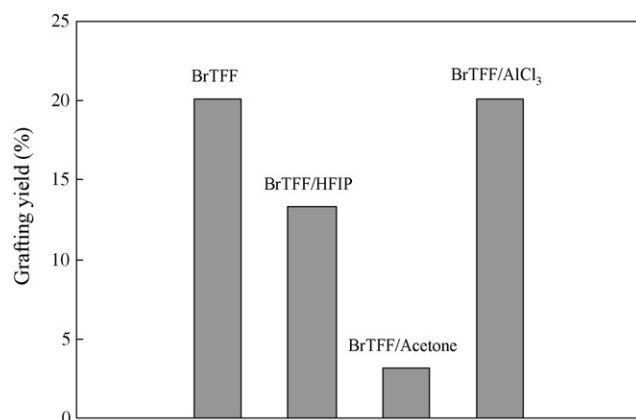


**Fig. 1.** The grafting yield of BrTFF into ETFE films as a function of doses in simultaneous irradiation at room temperature.

through the swollen grafted layer. It should be noted that this is the first example to proceed graft polymerization of perfluorinated vinyl ether into solid state polymer films to yield the poly(BrTFF) grafted ETFE film (ETFE-g-PBrTFF). The required dose for a satisfactory grafting yield such as 20% was as high as ca. 400 kGy, probably due to low polymerization reactivity of fluorinated monomers. Thus, to accelerate the graft reaction, the effect of solvents or catalysts on the grafting yield was examined in the following experiment.

It was reported that solvents or catalyst strongly influence the radiation-induced grafting of some monomers such as styrene or alkyl vinyl ether onto the base membranes [10,11]. Two compatible solvents, acetone and hexafluoroisopropanol (HFIP) to BrTFF were found. The effect of acetone and HFIP on the grafting yields of BrTFF into ETFE films is shown in Fig. 2. It was noticed that the GY decreased slightly after adding HFIP into grafting system, and the grafting was nearly to be inhibited in the presence of acetone. The Lewis acid,  $\text{AlCl}_3$  which is a reagent for converting radical species to cation in solid state graft polymerization, had almost no influence on the grafting reaction of BrTFF into ETFE films due to low solubility in BrTFF solution.

Grafting and homopolymerization of BrTFF may be initiated by different free radicals. It was reported when ETFE films are exposed to high energy radiation the initial reaction involves scission of C–F, C–H and C–C bonds leading to the formation of macroradicals, so in the presence of BrTFF monomer, these macroradicals in ETFE films will initiate graft copolymerization of BrTFF into ETFE films



**Fig. 2.** Effect of solvents and  $\text{AlCl}_3$  on the grafting of BrTFF into ETFE films. Grafting condition: BrTFF/solvent = 1/1 (w/w). Absorbed dose: 400 kGy; Room temperature.

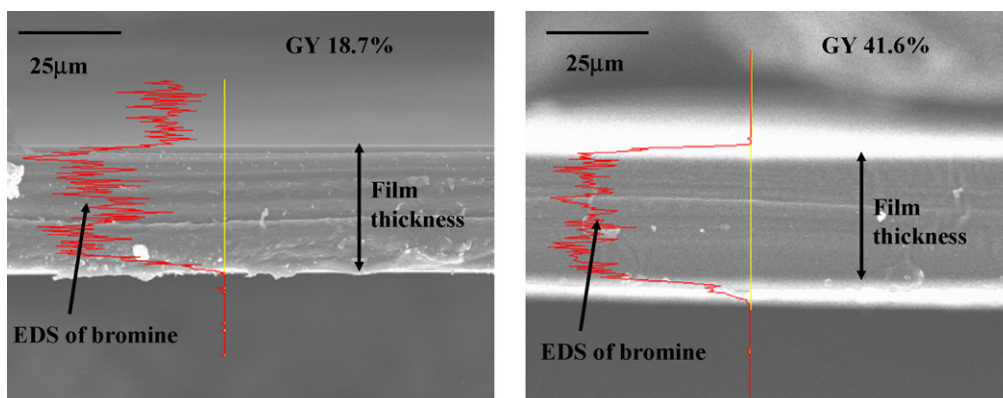
except for the formation of double bonds and crosslinking of ETFE itself [12,13]. Free radicals are also generated in BrTFF under the  $\gamma$ -rays irradiation as that of FVPE [4], which will initiate the homopolymerization of BrTFF. The grafting of BrTFF into ETFE films is controlled by the rate of BrTFF diffusion to the vicinity of the macroradicals of ETFE films. So some factors of grafting reaction such as monomer, solvent, dose, etc., directly affect the rate of grafting and homopolymerization; the above experimental results demonstrate this.

## 2.2. Graft penetration

The distribution of poly(BrTFF) grafts in the perpendicular direction of the ETFE film was characterized by scanning electron microscope connected with an energy distribution X-ray spectroscopy (SEM–EDS). Fig. 3 shows the SEM image and the EDS of bromine in the transverse plane of ETFE-g-PBrTFF film with GYs of 18.7 and 41.6%. It is obvious that poly(BrTFF) grafts homogeneously distribute into the ETFE film when the GY is more than 18.7%. Homogeneous grafting in a perpendicular direction to the film surface is favorable to further modified application such as brine electrolysis and fuel cells.

## 2.3. FTIR analysis of ETFE-g-PBrTFF films

Fig. 4 shows the FTIR spectra of the original ETFE and ETFE-g-PBrTFF films with different GY in the range  $700\text{--}1600\text{ cm}^{-1}$ . For an original ETFE film, the sharp absorption band at  $1454\text{ cm}^{-1}$  represents the CH deformation, whereas the strong absorption



**Fig. 3.** SEM image of the transverse plane of ETFE-g-PBrTFF films with EDS of bromine in the perpendicular direction.

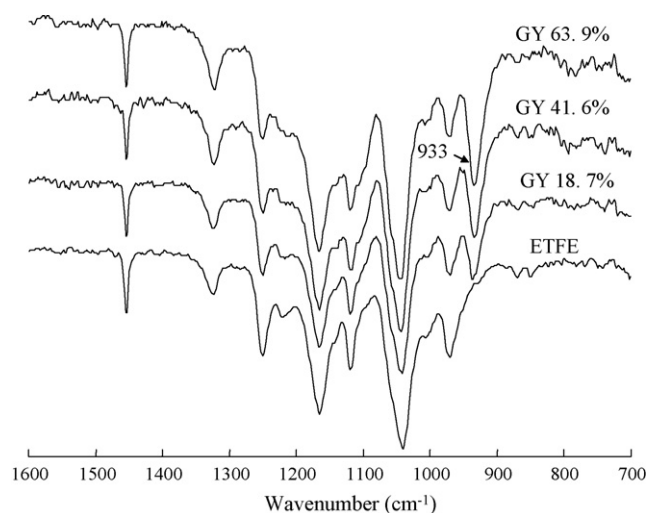


Fig. 4. FTIR spectra of original ETFE film and ETFE-g-PBrTFF films with different grafting yields.

bands in the range of 1000–1300  $\text{cm}^{-1}$  are assigned to the absorption of  $\text{CF}_2$  groups [13]. After grafting BrTFF into the film, FTIR spectrum of the ETFE-g-PBrTFF film showed a new absorption at 933  $\text{cm}^{-1}$ , and its intensity increased with the increases of GY, which is assigned to  $\text{OC}_2\text{F}_4\text{Br}$  group in a grafted BrTFF molecule as compared to the  $\text{OC}_3\text{F}_7$  group of FVPE [4].

#### 2.4. Thermal analyses

Fig. 5 shows the DSC curves of the original ETFE film and ETFE-g-PBrTFF films with different GY in the temperature range of 50–400  $^{\circ}\text{C}$ . The melting temperature ( $T_m$ ) showed a remarkable shift towards lower values compared to the original ETFE film with increasing GY. The heat of melting ( $\Delta H_m$ ) was evaluated from the area under the melting peaks. The degree of crystallinity (DC) was calculated using the following equation:

$$\text{DC} (\%) = \left[ \Delta H_m \times \frac{1 + \text{GY}\%}{\Delta H_{m100}} \right] \times 100 \quad (1)$$

where  $\Delta H_m$  is the heat of melting of ETFE films which is proportional to the area under the melting peak and  $\Delta H_{m100}$  is

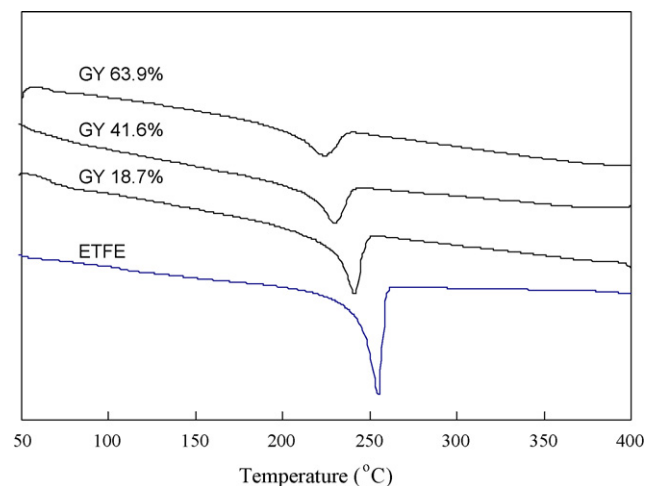


Fig. 5. DSC melting thermograms of original ETFE film and ETFE-g-PBrTFF films with different grafting yields.

Table 1  
 $T_m$ ,  $\Delta H_m$  and DC of neat ETFE and ETFE-g-PBrTFF films

Dose (kGy)	GY (%)	$T_m$ ( $^{\circ}\text{C}$ )	$\Delta H_m$ (J/g)	DC (%)
0	0	254.8	41.1	36.2
405	18.7	241.2	32.5	34.0
900	41.6	230.8	20.8	26.0
1230	63.9	224.2	17.2	24.9

the heat of melting of 100% crystalline ETFE polymer, which equals 113.4 J/g. [13]

The results were showed in Table 1. It was found that both  $\Delta H_m$  and DC decreased with increase in the dose or the GY. Usually, the grafting reaction of monomer is took place in the amorphous region of polymer matrix, which has no obvious influence on the DC. In this radiation-induced grafting system, the high dose was required for the grafting of BrTFF, which could induce the crosslinking of ETFE matrix. So it was thought about the decrease of both  $\Delta H_m$  and DC attributed mainly to radiation-induced crosslinking of ETFE matrix, which reduced the number and length of chains suitable for recrystallisation [12,13].

The TG thermograms were used to evaluate the thermal stability and homogeneity of ETFE-g-PBrTFF films. Fig. 6 shows the TG curves of the original ETFE film and ETFE-g-PBrTFF films with different GY in the temperature range of 25–550  $^{\circ}\text{C}$ . It was found that after grafting BrTFF there is only one-step degradation pattern similar to that of original ETFE. This is because poly(BrTFF) grafts have similar fluorinated structures with a base ETFE polymer; thus, the poly(BrTFF) grafts should be compatible to the amorphous phase of the ETFE films. The decomposition temperature obtained from the TG curve was defined as the point where the weight loss was 5%. As shown in Fig. 6, the decomposition temperature of the original ETFE film was 460  $^{\circ}\text{C}$ . The ETFE-g-PBrTFF with the GY of 18.7, 41.6 and 63.9%, showed the decomposition temperatures at 393, 366 and 340  $^{\circ}\text{C}$ , respectively. Namely, the decomposition temperatures decreased with increasing the dose or the GY. The decomposition temperature of ETFE chain in grafted ETFE film was clearly lower than that of original ETFE film maybe attributed to radiation-induced crosslinking and double bond formation in ETFE matrix, as that observed in grafted PTFE film [11]. Further, it can be also found that the grafted films yielded ca. 5% residual char at the final heating temperature of 550  $^{\circ}\text{C}$ , but the original ETFE film instead decomposed completely. In our past work, it was found that ETFE-grafted styrene derivatives films can decompose

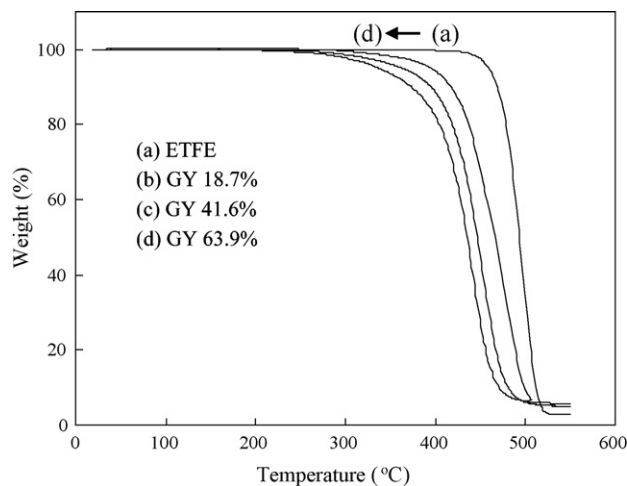


Fig. 6. TG thermograms of the original ETFE film and ETFE-g-PBrTFF films with different grafting yields.

completely [6]. These results suggest that the presence of bromine groups in the grafted film induced the carbonization during the thermal decomposition.

In conclusion, perfluorovinyl ether, BrTFF, could be grafted into the ETFE films by simultaneous  $\gamma$ -rays irradiation at room temperature. The irradiation with absorbed doses more than 400 kGy gave the poly(BrTFF) grafted ETFE membranes with grafting yields of more than 20%. It should be noted that this is the first example to proceed graft polymerization of perfluorinated vinyl ether into solid state polymer films. This simultaneous grafting of perfluorinated monomers will provide a new kind of method for the functionalization of perfluorovinyl compounds, and the resulting new-type fluorinated grafted films will be easily modified for further applications such as brine electrolysis membranes and polymer electrolyte membranes for fuel cells.

### 3. Experimental

#### 3.1. Materials

The ETFE film (25  $\mu\text{m}$ ) was kindly provided by Asahi Glass Co., Japan and was washed with acetone to remove any impurity on its surface before use. 2-Bromotetrafluoroethyl trifluorovinyl ether was purchased from Matrix Scientific Com. and used without further purification. Acetone, hexafluorobenzene (HFB), hexafluoroisopropanol and  $\text{AlCl}_3$  powder were purchased from Wako Pure Chemical Industries, Ltd., Japan.

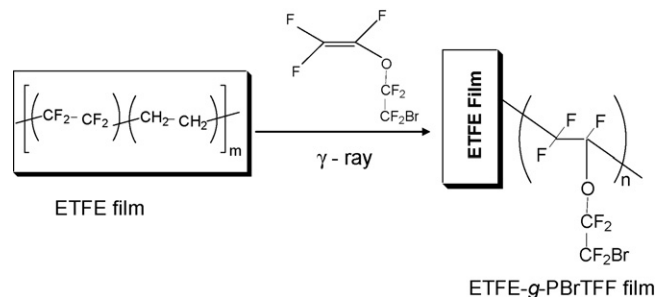
#### 3.2. Simultaneous radiation-induced grafting of BrTFF into ETFE films

The grafting reaction was carried out under the simultaneous irradiation of the ETFE and BrTFF monomer in an argon gas-filled ampoule (Scheme 1). For example, in a vacuum degassed 25 ml glass ampoule, ETFE with a size of 3 cm  $\times$  5 cm, and ca. 8 ml monomer and the solvent (HFIP, acetone) or 1 mg catalyst ( $\text{AlCl}_3$ ) was added. The argon gas was then bubbled and filled the ampoule.

$\gamma$ -Rays irradiation of the ampoule was performed in Co-60 source facility of Japan Atomic Energy Agency (JAEA) at room temperature with the dose rate of 15 kGy/h. After the designed absorbed dose, the film was transferred from the ampoule to a Soxhlet's apparatus and washed with HFB for 24 h to remove the ungrafted homopolymer and residual monomers. After drying to a constant weight in vacuum at 40  $^\circ\text{C}$ , the amount of the grafted polymer in the ETFE, namely grafting yield, was obtained as follows:

$$\text{GY} (\%) = \frac{m_1 - m_0}{m_0} \times 100 \quad (2)$$

where  $m_0$  and  $m_1$  are the weights before and after the grafting of BrTFF, respectively.



Scheme 1. Radiation-induced grafting of BrTFF into ETFE films.

#### 3.3. SEM-EDS analysis for graft penetration

The penetration of the poly(BrTFF) grafts into the ETFE film was investigated by determining the distribution of bromine in the transverse plane of the film with JEOL JSM-5600 SEM connected with EDS and operated at a voltage of 15 kV. The cross-section of the sample was prepared by cutting the films with a knife after immersion in liquid nitrogen, and subsequent coating with carbon.

#### 3.4. FTIR analysis

The attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectra of the films were recorded with a FTIR 710 (Horiba, Japan) equipped with a diamond ATR cell.

#### 3.5. Thermal analysis

The thermal properties were characterized by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) of the films using a Thermo Plus2/DSC8230 and a Thermo Plus2/TG-DTA (Rigaku, Japan). The specimen of ca. 5 mg was heated at a heating rate of 10  $^\circ\text{C}/\text{min}$ . The nitrogen flow rates through the specimen were 100 ml/min for the DSC and TG analysis.

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